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Procedia Engineering 44 (2012) 567 – 570

**Procedia  
Engineering**[www.elsevier.com/locate/procedia](http://www.elsevier.com/locate/procedia)**Euromembrane Conference 2012****[OD24]****Oxidative cleaning of reverse osmosis membrane used in the steel industry wastewater reclamation**H. Li\*, P. Yu, Y. Luo  
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Oxidative cleaning of reverse osmosis membranes fouled by steel industry secondary effluent has been investigated. The foulants were characterized by means of EDX and FTIR, and we found that the organics and metal oxide were deposited on the membrane surface. H<sub>2</sub>O<sub>2</sub> (pH=12.0) was selected to regenerate the fouled membrane. Considering the membrane resistance values, the cleaning kinetic was illustrated by Langmuir-Hinshelwood kinetics model.

**1. Introduction**

Although reverse osmosis (RO) is the current state-of-the-art water recycling technology, inherent membrane fouling is still the most important obstacle to the efficient application of membrane technology, particularly when it leads to the flux losses that cleaning cannot restore [1]. Membrane fouling behaviour could be illustrated by the resistance in series model as follows,

$$J = \frac{\Delta P}{\mu R} = \frac{\Delta P}{\mu(R_m + R_f)} \quad \text{----- (1)}$$

where J is the water permeate flux, ΔP is the transmembrane pressure, μ is the water viscosity, R is the total membrane resistance, R<sub>m</sub> is the intrinsic membrane resistance, R<sub>f</sub> is the fouling resistance.

Levitsky et al. [2] studied the oxidative cleaning mechanisms. However, the cleaning kinetics was not systematically addressed. In this study, the oxidative cleaning behaviour was described by Langmuir-Hinshelwood (L-H) kinetics model.

**2. Methods and Materials**

The fouled RO membrane element (Hydranautics, CPA2-4040) selected for the cleaning study had been in service for nearly 1.0 year in a steel plant. Membrane cleaning was performed with hydrogen peroxide solution at pH 12.0 by using a laboratory scale RO system. The foulants were detected by means of EDX and FTIR, and the cleaned membranes were characterized by means of SEM and ATR-FTIR.

**3. Results and discussion**

The fouling layer was characterized by the means of SEM-EDS and FTIR. The cross section SEM image in Fig.1 clearly confirms the formation of a cake layer on the membrane surface. Fig.2 shows the result that the amine and aliphatic acid are the dominant organic foulants in the

cake layer. Inorganic composition analyses (Fig. 3) indicates that metal oxides exist in the cake layer.

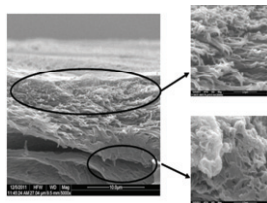


Fig. 1 SEM images of membrane of fouling layer

with 5,000 times

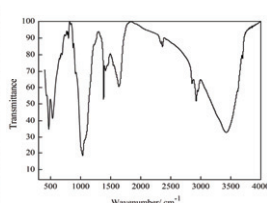


Fig. 2 FTIR spectra of physically

stripped fouling layer

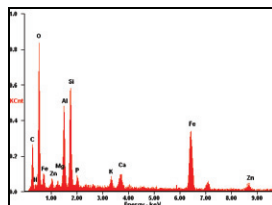


Fig. 3 EDS images

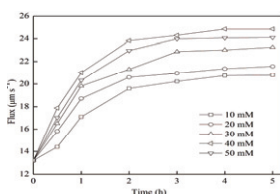


Fig. 4 Effect of concentration on the cleaning cleaning

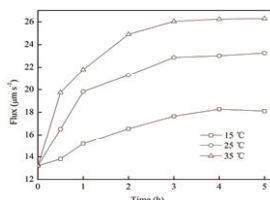


Fig. 5 Effect of temperature on the

The influences of operating parameters (concentration and temperature) on cleaning were evaluated and shown in Fig. 4 and Fig. 5. The flux increased firstly with the increasing  $\text{H}_2\text{O}_2$  concentration, and then it decreased at the concentration 50 mM. Temperature has a very significant effect on flux recovery. Increasing concentration and temperature increased the oxidative rate.

Cleaning is perhaps most frequently modelled as a first order reaction [3]. In this study, we propose the use of L-H kinetics rate model based on the membrane resistance decline because the cleaning reaction acts on the cake layer surface. This situation is in contrast to the research on the heterogeneous degradation of many organic contaminations [4]. The rate law is given by

$$r = k_c K c / (1 + K c) \quad (2)$$

Rearranging Eq. 2 leads to

$$\frac{1}{r} = \frac{1}{kK} \frac{1}{c} + \frac{1}{k} \quad (3)$$

where  $r$  is the initial rate of membrane resistance decline ( $\text{m}^{-1} \text{h}^{-1}$ ),  $k$  is the cleaning rate constant ( $\text{m}^{-1} \text{h}^{-1}$ ),  $c$  is  $\text{H}_2\text{O}_2$  concentration (mM),  $K$  is the Langmuir adsorption coefficient ( $\text{L mmol}^{-1}$ ).

As depicted in Fig. 6, the portion of the curve decreased in a straight line fashion with a related coefficient extremely near 1.0. It demonstrates that oxidative cleaning membrane quantitatively

corresponds to the L-H kinetics rate model. The temperature dependence of the cleaning constant  $k_c$  can be expressed by Arrhenius equation:

$$k_c = k_{c0} e^{-E_c/RT} \quad (4)$$

Eq. 2 becomes

$$\frac{r(1+Kc)}{Kc} = k_{c0} e^{-E_c/RT} \quad (5)$$

where  $E$  is apparent activation energy of cleaning,  $k_{c0}$  is the kinetic cleaning power of oxidative cleaning formulations and processes,  $T$  is cleaning temperature.

Let  $\alpha = r(1+Kc)/Kc$ ,  $a = E/R$ ,  $b = \ln k_{c0}$ . Rearranging Eq. 5 leads to

$$\ln \alpha = b - a \frac{1}{T} \quad (6)$$

A semi-log plot of  $(\alpha)$  vs. reciprocal temperature provides a straight line (Fig. 7). The analysis assumes that the oxidative cleaning process follows the L-H kinetics before cleaning solution concentration reached the maximum value. This accounts for the oxidation of the fouling layer.

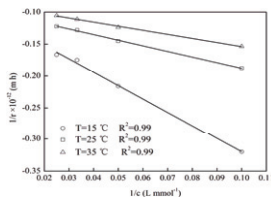


Fig.6 Reciprocal the initial cleaning rate vs. reciprocal cleaning temperature

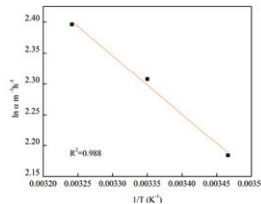


Fig. 7 Semi-log plot of  $\alpha$  vs. reciprocal

$H_2O_2$  concentration

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Keywords: Oxidative cleaning, reverse osmosis membranes, Langmuir-Hinshelwood kinetics model, Arrhenius equation

